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BENEFICIATION OF THAL SILICA SAND AND THE PRODUCTION OF HIGH GRADE SILICON PARTICLES

T. Ahmad[1]*, M. Kamran[1], B.A. Wahjoedi[2], M.T.Z. Butt, U. Manzoor[1], Z. Abbas[1]
[1]Department of Metallurgy and Materials Engineering, College of Engineering and Emerging Technologies, University of the Punjab, Lahore, Pakistan
[2]Department of Fundament and Applied Sciences Universiti Teknologi, Petronas, Malaysia

Abstract

Silica sand from Bita site of THAL desert, situated in Punjab province of Pakistan was processed to produce nanoparticles using a ball mill. The produced nanoparticles of silica sand were verified using Zetasizer nanoparticles analyzer. It was observed that the ball milling process not only reduced the particle size but also librated the silica particles from the impurities resulting in increased purity of silica in Thal silica sand from 86.60 wt. % to 95.52 wt. % as major impurities consisting of Al_2O_3 and CaO, were liberated during grinding and separated during sieve analysis process. The leaching of silica sand nanoparticles with a mixture of HCl and CH_3COOH further improved the weight percentage (wt.%) purity of silica in Thal silica sand up to 96.60 wt.%.

The beneficiated Thal silica sand nanoparticles were then reduced with Magnesium to produce silicon particles at 900°C with and without the presence of argon atmosphere. The production of silicon particles during reduction was verified with XRD analysis and FESEM with EDX analysis. It was observed that the presence of argon atmosphere during reduction of silica sand nanoparticles increased the wt. % of reduced silicon in processed sample. The leaching of reduced samples with a mixture of HF and CH_3COOH further improved its purity.

Keywords: Thal Silica Sand, nanoparticles production, reduction, XRD analysis, Silicon particles

1. Introduction

Silica contributes 2/3 proportion of the earth crust and exists in polymorphs in which quartz and quartzite are most pure forms. The most common impurities found associated with silica minerals are CaO and Al_2O_3. The Sand which is being used for the purpose other than construction, is referred to as silica sand or industrial sand because of high silica contents it has [1]. Beneficiation studies to librates minerals from their associated gangue materials usually involve crushing and grinding and classification processes involving usually a

* Corresponding Author: tahirengg4051@yahoo.com

combination of sieving and concentration processes, such as electromagnetic separation, froth floatation etc. Different combinations of these processes have been studied exploiting different characteristics of minerals and gangue material in an ore. Ozan *et al.* [2] used synthetic mixture of tungsten and quartz to mimic a gold ore to optimize operating parameters such as bowl speed, solid feed rate and air fluidizing pressure of a laboratory scale Knelson Concentrator for a dry feed flidized with air to achieve highest grade and recovery. A rare earth ore was beneficiated by Adam *et al.* [3] using a wet high intensity magnetic separation (WHIMS) in conjunction with gravity pre-concentration steps (Knelson and Falcon centrifugal concentrators) and XRD analysis of the WHIMS first concentrate (lowest applied magnetic field strength) obtained from Falcon concentrate showed the ferromagnetic iron oxide gangue minerals in the RE ore may potentially be removed from a gravity concentrate using low intensity magnetic separation.. Similarly beneficiations of a complex rare earth element (REE) ore containing REE minerals of carbonates, silicates and oxides and other REE bearing minerals (e.g. zircon and pyrochlore etc.) by flotation and high gradient magnetic separation (HGMS) process resulted in concentrates with over 95% recovery of carbonates with three major REE minerals bastnaesite, parisite and synchysite over 96 % and the silicate REE minerals such as cerite (Ce) and allanite up to 86% and 65%, respectively Xiaosheng *et al.* [4]. Alex *et al.* [5] conducted a comparative study of two dry grinding schemes to optimize energy consumption to process a commercial aggregate as feed material and reported that a high pressure grinding roll (HPGR) in closed circuit with air classification requires 20.8–29.5% less energy per tonne as compared to using HPGR in closed circuit with a 2.36 mm screen, followed by a locked-cycle Bond test. The material moisture, and effect of discharge recycle ratio on the product quality and pellet feed applications on High Pressure Grinding Roll (HPGR) operation was studied by Frank *et al.* [6] and final grinding in iron ore pellet feed preparation using HPGR and air classification was also highlighted. The alteration of the crystalline regularity of the silica sand during mechanical milling method and carbothermal nitridation process with Taguchi's to produce silicon nitride and silicon carbide whiskers verified by Taguchi's signal to noise ratio and variance techniques suggested that The duration of the mechanical milling, followed by temperature, time and heating rate were the important factors influencing the formation of silicon carbide Mustapha *et al.* [7]. As concerned with the SiO2 beneficiation and its reduction to Si, Dietl *et al*. [8] determined that quartz and quartzite as two main sources of silicon raw materials for photovoltaic application as their rocks are most stable and exist in pure form that can be found in almost all mineralogical rocks. Optimization of processes for purification of SiO_2 and its reduction to Si is very much important for solar energy to compete the worldwide increased demand of cheaper renewable energy source. One of the issues that limited the use of solar energy is the high cost of materials associated with solar cell manufacturing particularly the cost of silicon, being the most essential raw materials in the photovoltaic industry Swanson *et al.* [9]. Feasibility of metallurgical grade silicon up to the solar grade was performed by Yuge *et al.* [10] using plasma furnace for boron removal and electron beam furnace for phosphorus removal to less than one part per million (ppm), a basic requirement for solar cell grade silicon.. The purification of silicon during the solidification was also studied Takeshi *et al.* [11]. Larbi et al. (2010) studied the production of high grade silicon by leaching rice husk to obtain SiO_2 and reduction with Mg at different temperature to produce silicon powder. Going through the previous research it was found that some of the researchers such as Tahir *et al.* [12] had produced silica sand nanoparticles from local sand but still no work was found to produce silicon particles from local sand especially reduction with Magnesium (Mg) metal. Therefore, this

research is intended to fill this gap and to produce high grade silicon particles from local silica sand.

2. Materials and Methods

2.1. Materials

The samples of silica sand were collected from Thal desert located in the Punjab province of Pakistan. It is near the Pothohar Plateau between Sindh and the Jhelum rivers. It extends 280Km from North to South in length with 110 km [13]. Silica sand Samples were collected from four different areas one Km apart from each other and were taken one to two feet deep from surface level. A known amount of collected samples of silica sand was mixed with water and stirred for 20-30 minutes to allow/confirm complete dissolution of mud and other soluble impurities. The residue (silica sand) was collected after filtration. The residue of silica sand was then dried in electric oven for 2 to 3 hours at 120^{o}C. Silica sand was sieved using Endicott's Octagon 200 Sieve shaker with different sieves calibrated according to British standards was used to get different particles size having mesh numbers such as 100, 140, 200, 270, 400 etc. and each fraction was stored in air tight polythene bags. Maximum weight retained having 212µm of silica sand was picked for the production of silica nanoparticles. Grinding of silica sand samples was done in ball mill at 90 rpm with 140 zirconia balls (each ball was 12.5gm in weight and 1.5cm in diameter) for 5 hours keeping materials to balls ratio 3:1. The milled silica sand was then sieved to get particles size less than 38µm. This silica sand was again ground in ball mill for one hour to get Nano sized silica sand particles.

2.2 Methods

Silica sand collected from Thal desert was analyzed for chemical composition using X-ray fluorescence (XRF) and the nanoparticles size was verified using Zeta sizer nanoparticles analyzer. FESEM (Field Emission Electron Microscope) was used to characterize the particle morphologies. Philips diffraction meter XRD (model PW 3710) with X'PERT graphics software package was used to analyze the structures of the silica sand. To increase the purity of silica in silica sand acid leaching was performed. The leaching of silica sand was carried out with 5g of silica sand in 10 wt. % solution containing hydrochloric acid (HCl) and acetic acid (CH_3COOH) in volume ratio of 4:1 respectively in 2 liter Teflon beaker for 2 hour at room temperature. The residue was thoroughly washed with cold deionized water. The residue obtain on the filter paper is dried at 100^{o}C for 1 hour. 5 grams of silica sand and 4 grams of magnesium were mixed with 4% solution of polyvinyl alcohol (binding agent) and heated at 110^{o}C for 15 min to remove the volatile components. Silica sand nanoparticles and magnesium mixture was compacted using a hand operated hydraulic press with 4500 kg load for 3 min. The reduction of silica sand nanoparticles with magnesium was carried out at 900°C for 1 hour with and without argon atmosphere in Nobertherm Tube Furnace with maximum temperature range 1600°C. The reduced silicon particles were analyzed using XRD and FESEM with EDX analysis. A similar method of leaching and reduction was adopted by Larbi et al. (2010) to produce silica and silicon from rice husk. The leaching of reduced silicon particles was also carried out in 4.8 wt. % HF: 25 wt.% CH_3COOH acid mixture in a volume ratio of (1:9) respectively. The acetic acid was introduced first and shortly followed by the HF acid. Leaching at each cycle was carried out at 70 °C for duration of one hour. In between cycles, the leached slurry was filtered using filter

paper (Whatman # 42) applying a vacuum assisted filtration assembly and washed with water. The leached samples were dried and analyzed with XRD and FESEM.

3. Results and Discussion

3.1 Silica sand Particles characterization

The collected silica sand from Thal desert was washed with water and analyzed using sieve analysis as shown in Table 1. The maximum weight retained at 212µm size was 849.50g which was further utilized for grinding.

Table 1. Sieve analysis of Thal Silica Sand.

Sr. No.	Mesh No.	Aperture Size (µm)	Weight Retained (Grams)
1.	20	850	0.268
2.	30	600	0.302
3.	40	425	15.733
4.	50	300	173.677
5.	70	212	849.502
6.	100	150	640.571
7.	140	106	410.750
8.	200	75	168.171
9.	270	53	108.026
10.	400	38	39.904

3.2 FESEM and EDX analysis of Thal Silica Sand

Thal Silica Sand particles were analyzed using FESEM and the particles are found to be in different shapes as shown in Figure 1(a). EDX analysis of natural silica sand is shown in Figure 1 (b) and it was observed that Thal silica sand consist of major oxides of silica, alumina and calcium oxide. The element composition of Thal silica sand and silica sand nanoparticles is shown in Table 2.

Table 2. Chemical Composition of Thal Sand and silica sand nanoparticles (EDX)

Compound	O	Na	Mg	Al	Si	K	Ca	Fe
Wt.% of Natural silica sand	47.86	1.80	1.26	6.67	30.45	2.11	7.85	1.99
Wt.% of silica sand Nanoparticles	44.19	0.04	0.03	1.53	50.32	0.07	2.41	1.55

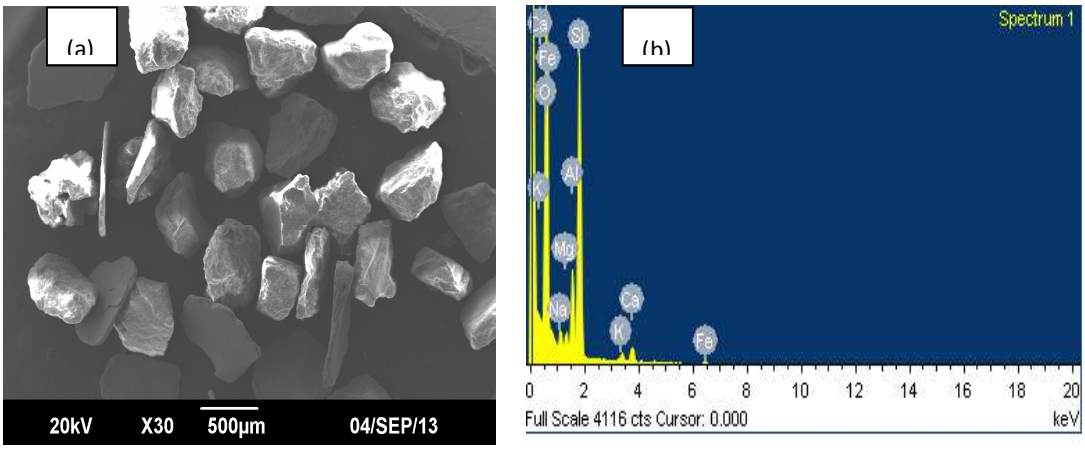

Figure 1. (a) FESEM, (b) EDX analysis of Thal Silica Sand.

EDX analysis shown in Table 2 indicated that wt.% of silica is improved during grinding process because the hard compounds such as Al_2O_3 and CaO are liberated during grinding and sieving process.

3.3 Analysis of Nanoparticles of Thal Silica Sand

The nanoparticles of Thal silica Sand was analyzed using Zetasizer and the results are shown in Figure 2. The average particles size was in the rage of 74 nm.

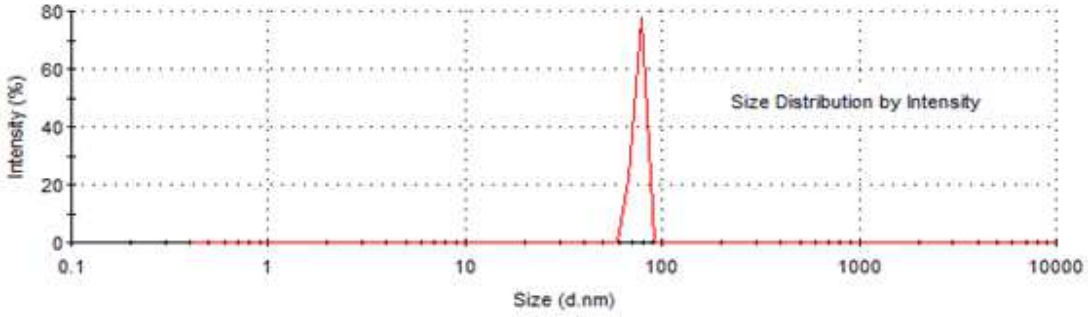

Figure 2. Average particle size of Silica Sand by size distribution.

3.4 FESEM micrograph and EDX analysis of Silica sand Nanoparticles after grinding process

The silica sand nanoparticles are agglomerated shown in Figure 3(a). At nano-level a large tendency of agglomeration, segregations of particles is observed at higher magnification. EDX analysis of silica sand nanoparticles showed the increasing content of silica in sand. During grinding it was found that alumina and calcium oxide are separated because of their high hardness. Figure 3 (b) showed the EDX analysis of silica sand nanoparticles. The same beneficiated Thal Silica Sand nanoparticles were used by Tahir *et al.* [12] to produce epoxy

based hybrid composites and to study the effect of Thal silica sand nanoparticles and glass fiber reinforcements on epoxy-based hybrid composite.

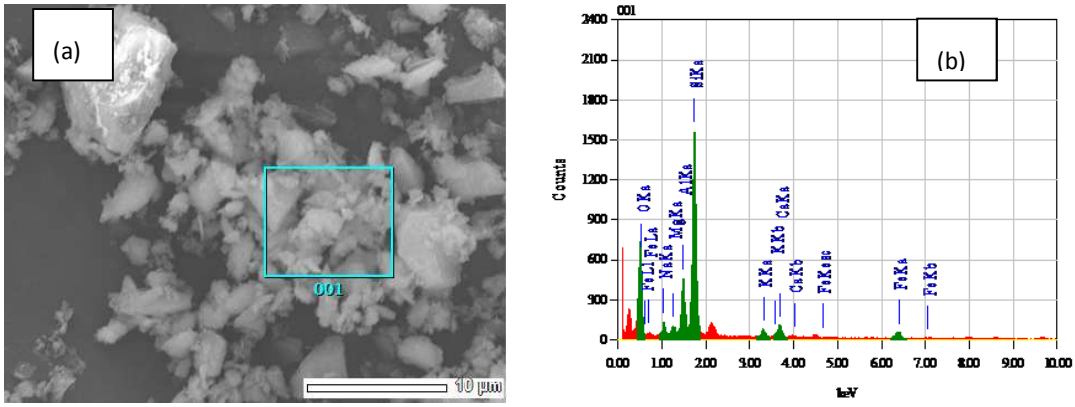

Figure 3. (a) FESEM, (b) EDX analysis of silica sand nanoparticles.

3.5 XRF Analysis of Thal Silica Sand, Silica sand nanoparticles and leached Silica Sand (wt. %)

The silica sand as obtained from Thal Desert area as well as the sand obtained after milling process was also analyzed using XRF for comparison. It was found that the natural silica sand contains 86.60wt.% of SiO_2 in it. The XRF test results of silica sand nanoparticles after grinding are shown in table 3. It can be observed that during the grinding process the wt. % purity of silica in Thal silica sand was increased. Silica sand contained Al_2O_3 and CaO as second large constituents which are harder as compared to silica and liberated during grinding and separated out by sieve analysis. The XRF test results of silica sand nanoparticles which were leached with of HCl and CH_3COOH solution showed that the leaching process further increased the wt.% purity of silica in Thal silica sand and is upgraded to a level of 96.60 wt.% as shown in table 3. In leaching process the formations of chlorides helps to separate out impurities during filtration.

Table 3. Chemical Composition (Wt. %) of Thal sand, Silica sand nanoparticles and leached Sand

Compound	SiO_2	Al_2O_3	K_2O	CaO	TiO_2	Cr_2O_3	Fe_2O_3	MnO
Natural Silica sand	86.60	3.30	1.30	6.51	0.80	0.23	1.10	0.18
Silica sand Nanoparticles	95.52	1.71	0.52	1.30	0.44	0.23	0.56	0.11
leached silica nanoparticles	96.60	1.20	0.29	0.90	0.25	0.13	0.40	0.09

3.6 XRD Analysis of Thal Silica Sand

The XRD graph of untreated sample of Thal Sand showed that the highest peak intensity was observed for (101) plane at 2θ of 26.877. The XRD analysis identified the values of full width half maxima (FWHM), d-spacing and crystalline size for the (101) plane as a highest peak. The peaks of other plans of silica were also indentified by XRD at different angles as shown in Figure 4.

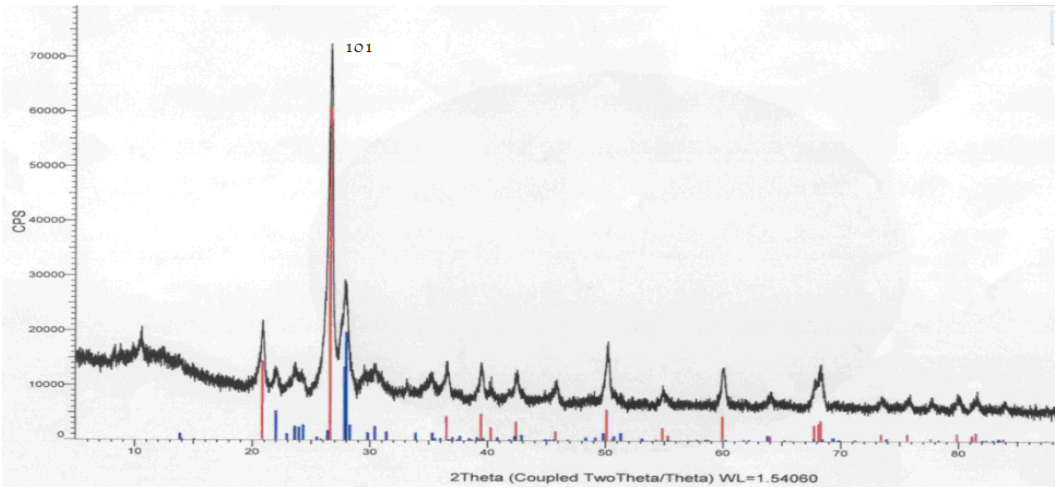

Figure 4. XRD Analysis of the Thal Silica Sand.

3.7 XRD Analysis of reduced Silicon with and without Argon atmosphere

The XRD results of Mg reduced of silica sand nanoparticles without argon are shown in Figure 5. More than 75 wt. % of silicon was observed without argon atmosphere using single zone tube furnace at constant temperature of 900^{o}C. Four strong peaks of silicon at 2θ of 28.44^{o}, 47.30^{o}, 56.12^{o}, 69.13^{o} and 76.38^{o} were indicated by XRD results. The peaks are at similar angle of 2θ for standard peaks of silicon as discussed by Larbi *et al.* [14]. Some other peaks at 2θ of 36.94^{o}, 42.97^{o}and 62.40^{o} are indicating the formation of magnesium oxide and magnesium silicate (Mg_2SiO_4).

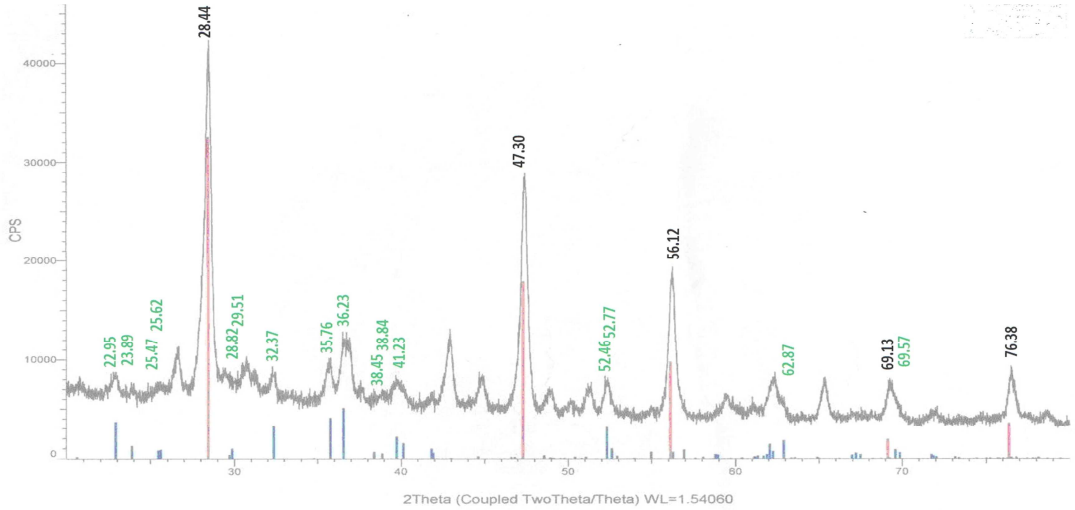

Figure 5. XRD analysis of silica sand without Argon at 900^{o}C.

To improve the quality of silicon, Silica sand was again reduced with Mg under argon atmosphere at constant temperature 900^{o}C. The reduced silicon powder was further leached with 4.8 wt. % HF: 25 wt. % CH_3COOH acid mixture in a volume ratio of (1:9) respectively. The XRD analysis is shown in the Figure. 6. It was found that the reduction in argon atmosphere and leaching with a mixture of HF and CH_3COOH improved the wt. % of silicon and that quantity was more than 90.24wt. % as shown in Figure 7. Many peaks at 2θ of 28.44^{o}, 47.30^{o}, 56.12^{o}, 69.13^{o} and 76.38^{o}of were observed by XRD results. The peaks are at similar angle of 2θ for standard peaks of silicon as discussed by Larbi *et al.* [14]. Some other peaks at 2θ of 21.94^{o,} 22.97^{o}and 27.97^{o} are indicating the formation of magnesium oxide and magnesium silicate (Mg_2SiO_4).

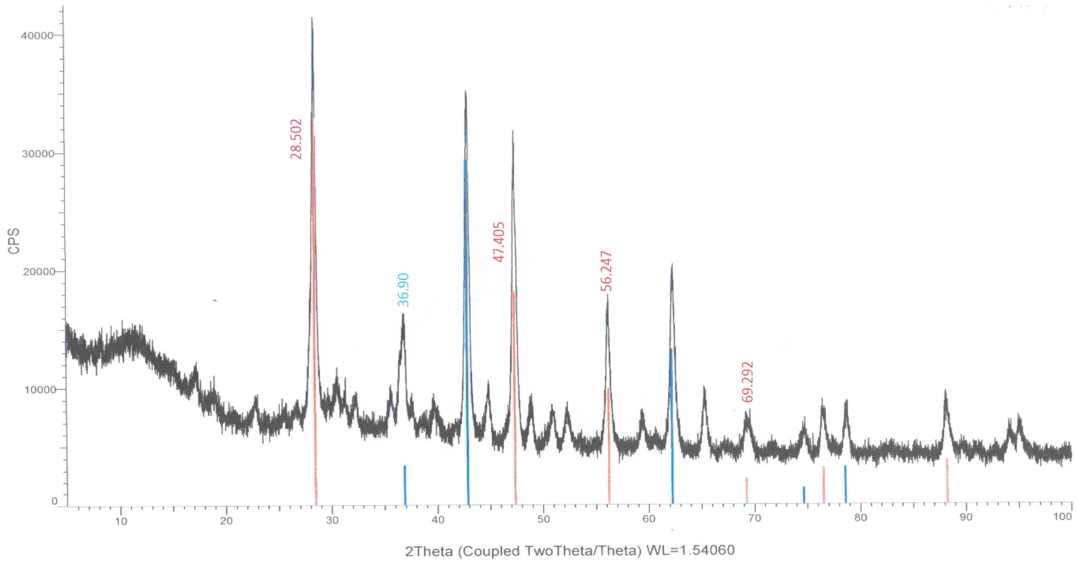

Figure 6. XRD analysis of silica sand under Argon at 900^{o}C.

3.8 FESEM and EDX Analysis of reduced and leached Silicon Powder

The leached silicon powder was analyzed using FESEM analysis as shown in Figure 7 (a) and EDX analysis showed the highest peaks of silicon as shown in Figure 7 (b). The presence of oxygen is due to oxides of SiO_2, CaO and Al_2O_3 present in reduced samples as shown in Table 4.

Table 4. EDX analysis of reduced and leached Silicon powder

Element	Si	Mg	Al	K	O	Ca	Na
			.90	0.37	6.33	0.20	0.31
			0.60	0.56	2.47	0.91	0.62

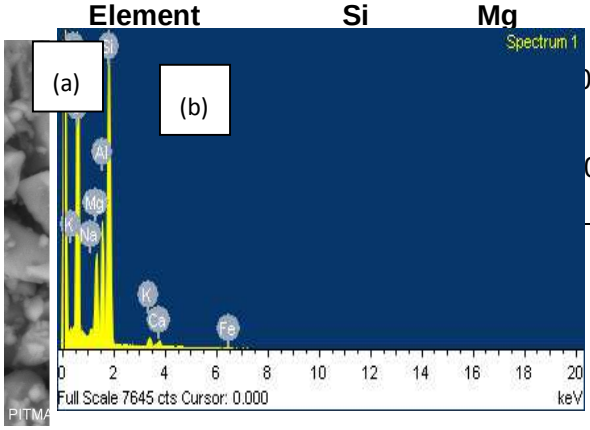

Figure 7. (a) FESEM, (b) EDX analysis of leached silicon powder.

4. Conclusions

The silica sand collected from different parts of Thal desert was successfully grounded to nanoparticles using a ball mill. The production of nanoparticles of silica sand was verified using Zetasizer analyzer and average particles size was found to be 74.00 nm. It was observed that the ball milling process also enhanced the wt. % purity of silica in Thal silica sand from 86.60 wt. % to 95.52 wt. %. The major impurities in Thal silica sand were found to be Al_2O_3 and CaO and were separated during grinding and sieving operations. The leaching of silica sand with a mixture of HCl and CH_3COOH, also improved the wt. % purity of silica in Thal silica sand up to 96.60 wt. %.

Thal silica sand was reduced with Magnesium at 900^oC with and without the presence of argon atmosphere. The presence of argon atmosphere during reduction of silica sand with Mg and leaching with a mixture of acid improved the wt. % of silicon up to 90.24 wt. %. The XRD results of reduced samples of silica sand with Mg confirmed the strong peaks of silicon and these peaks are verified with the standard peaks of silicon particles.

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